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SYNTHESIS, STRUCTURE, AND PROPERTIES OF TITANIUM CARBOSILICIDES FROM MATERIALS FROM THE FeSi – Ti – C SYSTEM

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The possibility of obtaining titanium carbosilicides by self-propagating high-temperature synthesis from materials based on the FeSi – Ti – C system was demonstrated. The microstructure and phase composition of the synthesized materials Ti_3SiC_2 and $Ti_5Si_3C_x$ ($x < 1$), were investigated.

Key words: self-propagating high-temperature synthesis, titanium carbosilicides, phase composition, microstructure, conductance.

In the last ten years, fire-resistant and heat-resistant materials based on titanium have attracted the attention of researchers. The family of so-called MAX-compounds corresponding to the formula $M_{n+1}AX_n$, where M is a transition metal, A is a group IIIA or IVA element, and X is carbon or nitrogen, are comparatively new materials [1]. Titanium carbosilicide, Ti_3SiC_2, is one of the most promising of this class of compound.

This compound has a hexagonal crystal lattice in which every three closely packed layers of titanium atoms alternate with one layer of silicon atoms, while carbon atoms occupy the octahedral pores between the titanium atoms. As a result, the unit cell of Ti_3SiC_2 acquires a laminate (nanolaminate) structure. The lamination gives Ti_3SiC_2 unique mechanical characteristics: microplasticity (10^{-4}), high elastic (326 GPa) and shear (135 GPa) moduli, failure viscosity ($7 – 12$ MPa $\cdot$ m$^{0.5}$), strength, crack resistance, and thermal stability. The material has good thermal and electric conduction, and chemical stability, and can be mechanically processed, which creates prospects for using it in materials for high-temperature and electrical applications, especially in production of items of complex shape [1, 2].

However, despite the uniqueness of the useful and practical relationship of the properties, Ti_3SiC_2 has not been widely used in materials science up to now. One factor that has held back the wide use of Ti_3SiC_2 is the complexity of obtaining it in the form of a single-phase product. Two methods of obtaining Ti_3SiC_2 materials are basically used: heterophase synthesis from titanium carbide and reactive sintering in the Ti?SiC?C system. In both cases, the synthesized material contains TiC, Ti_5Si_3, and Ti_sSi_2 in addition to the basic phase, which decreases its physical and mechanical properties.

The analysis of the existing methods of synthesis of Ti_3SiC_2 shows that the basic cause of the non-single-phase character of the synthesized product consists of disturbance of the initial stoichiometry caused by evaporation of silicon from the reaction mixture. One method of reducing losses of silicon in the reaction mixture is to use it not in the form of pure elemental powder but in the form of compounds.

We investigated the phase composition, microstructure, and some properties of products obtained by self-propagating high-temperature synthesis (SHS) in the FeSi – Ti – C system.

FeSi (FS-75), Ti (PTS), and carbon black (PM-15) powders were used to prepare the reaction mixtures. The products of synthesis were investigated by x-ray phase (DRON-2), micro-x-ray spectral (CAMECA), and microstructural (AXIOVERT 200M) analyses.

The samples for the electric-conducting coatings were prepared by mixing the powder of the synthesized product with a polymer solution. The suspension was applied on ceramic substrates with metal electrodes. Then the samples were gradually annealed at temperatures from room temperature to 350°C.

According to the published data [2], there are two ternary compounds in the Ti – Si – C system: Ti_3SiC_2 and $Ti_5Si_3C_x$ ($x < 1$). It is interesting to compare the analysis of the materials based on Ti_3SiC_2 and $Ti_5Si_3C_x$ obtained by SHS using

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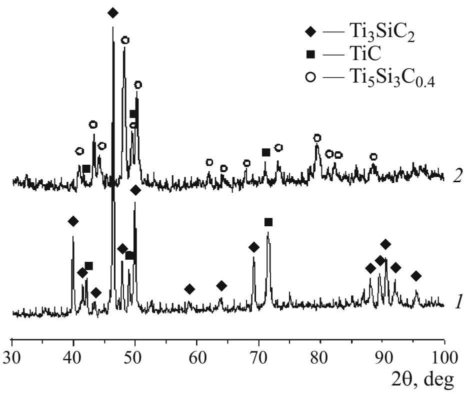

Fig. 1. Diffractograms of SH-synthesized samples: *1*) mixture calculated for obtaining Ti_3SiC_2; *2*) mixture calculated for obtaining $Ti_5Si_3C_x$.

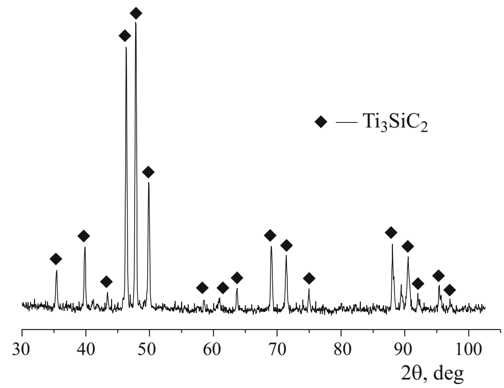

Fig. 3. Diffractogram of the sample synthesized by SHS from a mixture of Ti, SiC, and C powders of stoichiometric composition corresponding to the compound Ti_3SiC_2.

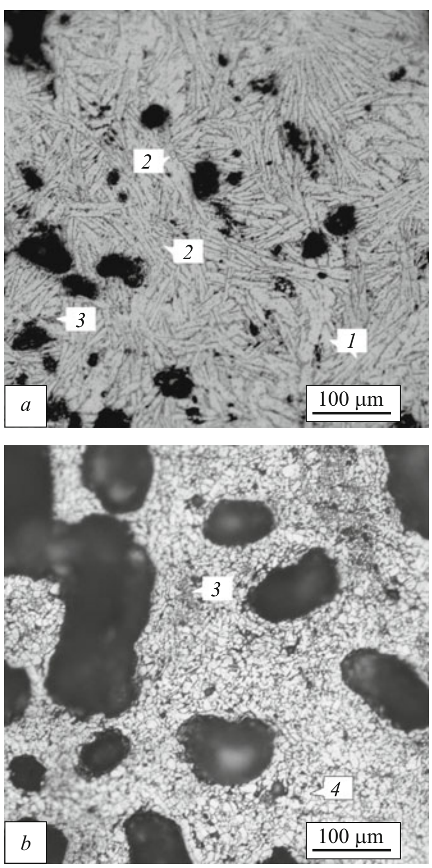

Fig. 2. Microstructure of the sample based on Ti_3SiC_2 (*a*) and $Ti_5Si_3C_x$ (*b*): *1*) Ti_3SiC_2; *2*) TiC; *3*) Fe-based phase; *4*) $Ti_5Si_3C_x$.

FC-75 ferrosilicium powder as the silicon-containing reagent.

The results of the x-ray phase analysis (Fig. 1) show that in x-ray pattern *1* where the basic compound is Ti_3SiC_2, there are also reflections belonging to TiC. There is basic compound $Ti_5Si_3C_x$ in x-ray pattern *2*, as well as peaks belonging to TiC. In addition, all x-ray patterns exhibit weak reflections which could not be interpreted with the JCPDS card index. As a function of the composition of the initial mixture, SHS can thus be used to synthesize products with Ti_3SiC_2 or $Ti_5Si_3C_x$ in the basic phases. The materials synthesized by SHS contain no silicides, which is the advantage of this method over others.

The microstructure of the synthesized sample based on Ti_3SiC_2 is shown in Fig. 2*a*. Ti_3SiC_2 is the basic phase and can have the appearance of elongated flakes. In addition to this phase, a grey-colored phase in the form of small round particles — titanium carbide — was also identified.

The microstructure of the $Ti_5Si_3C_x$ sample is shown in Fig. 2*b*. In contrast to Ti_3SiC_2, the grains of $Ti_5Si_3C_x$ do not have pronounced faceting.

In addition to the indicated phases, the microstructure of the synthesized products also has another structural constituent which consists of Ti, Fe, and Si according to the data from local micro-x-ray spectral analysis. We can hypothesize that the weak, unidentified reflections in the diffractograms in Fig. 1 belong to this phase.

The microhardness of Ti_3SiC_2 and $Ti_5Si_3C_x$ was measured with a 20 g load. The microhardness of Ti_3SiC_2 was $H_\mu = 76.7$ GPa and that of $Ti_5Si_3C_x$ was $H_\mu = 11.0$ GPa. It follows from the microhardness measurements that Ti_3SiC_2 is a more plastic compound than $Ti_5Si_3C_x$, since radial cracks, indicating the brittleness of the compound, were observed in measuring the microhardness of $Ti_5Si_3C_x$ from the angles of the indenter impressions.

Since loss of silicon to the reaction mixture is the basic cause that makes it difficult to obtain a single-phase product, microstructural and x-ray phase studies of the initial products with a different FeSi content were conducted with SHS. The studies showed that the initial composition with a FeSi content 15% higher than for the stoichiometric composition of Ti_3SiC_2 is optimum. In this case, the synthesized sample contains the highest amount of Ti_3SiC_2 phase and insignificant amounts of other phases.

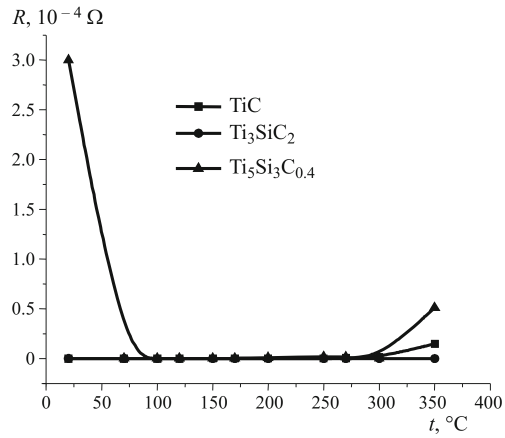

Fig. 4. Electric resistance of different phases as a function of coating formation temperature.

The use of ferrosilicium causes the appearance of an iron-containing phase in the products of synthesis. A single-phase product can be obtained in substituting ferrosilicium in the initial mixture by silicon carbide followed by high-temperature treatment of the products of synthesis (Fig. 3).

The Ti_3SiC_2 and $Ti_5Si_3C_x$ materials were used as fillers in resistive suspensions for film heaters as an alternative to titanium carbide. Film heaters are more economical and efficient heat sources than classic electric tube heaters. However, the currently used film heaters are low-temperature heaters, which limits the area of their application basically to household IR radiators.

On the example of conducting coatings where copper [3] and nickel [4] were the filler, it was shown that the increase in the electric resistance of the coatings at temperatures above 350°C is due to oxidative degradation of the polymer matrix and formation of a barrier layer of copper and nickel oxides on the surface of the filler particles, which prevents passage of an electric current between particles. The stability of the electrical properties is directly dependent on the resistance of the filler material to oxidation.

The curve of the electric resistance as a function of the temperature for the different phases is shown in Fig. 4.

The electric resistance of the coatings containing Ti_3SiC_2 almost does not change up to the temperature of 350°C. While the resistance of the coatings containing titanium carbide and $Ti_5Si_3C_x$ increases sharply at temperatures above 300°C. According to the published data [5], Ti_3SiC_2 has the highest resistance to oxidation (initial oxidation temperature of 850°C for TiC and 1370°C for Ti_3SiC_2). The Ti_3SiC_2 ceramic with a nanolaminate structure is thus the preferred material for film heaters based on the results of our studies.

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